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**FIRE RETARDANT COMPOSITION**

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 US4097630  
 JP58041972  
 US3770577**Abstract of WO8700852**

A coating composition suitable for application to a substrate for curing thereon to form a fire-retardant coating, the composition being formed of a mixture of an aqueous emulsion of ethylene-vinyl chloride copolymer, the ratio of the dry weight of the copolymer to one hundred parts of the composition being in the range between about 15 to 17 parts; a powder of either zinc borate or a mixture of aluminum trihydrate and zinc borate in a weight ratio of from about 4.5 to 35 parts per hundred of the composition, the weight ratio of zinc borate to aluminum trihydrate being not less than 1:6; added water in an amount between 30 and 45 parts per hundred of the composition; a thickening agent present in amount sufficient to maintain the powder in suspension; and a dispersing agent present in sufficient amount to impart fluidity to the composition and to enhance dispersion of the powder in the composition.

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<b>(21) International Application Number:</b> PCT/US86/01614 <b>(22) International Filing Date:</b> 5 August 1986 (05.08.86) <b>(31) Priority Application Number:</b> 764,186 <b>(32) Priority Date:</b> 9 August 1985 (09.08.85) <b>(33) Priority Country:</b> US <b>(71) Applicant:</b> FIBER MATERIALS, INC. [US/US]; Biddeford Industrial Park, Biddeford, ME 04005 (US). <b>(72) Inventors:</b> HILL, John, E., Jr. ; 360 South Street, Biddeford, ME 04005 (US). STEPHENSON, John, Scott ; 506 Preble Street, South Portland, ME 04106 (US). <b>(74) Agent:</b> SCHILLER, Robert, J.; Schiller & Pandiscio, 60 Hickory Drive, Waltham, MA 02154 (US).		<b>(81) Designated States:</b> DE, FR (European patent), GB, JP.  <b>Published</b> <i>With international search report.</i>
<b>(54) Title:</b> FIRE RETARDANT COMPOSITION  <b>(57) Abstract</b> <p>A coating composition suitable for application to a substrate for curing thereon to form a fire-retardant coating, the composition being formed of a mixture of an aqueous emulsion of ethylene-vinyl chloride copolymer, the ratio of the dry weight of the copolymer to one hundred parts of the composition being in the range between about 15 to 17 parts; a powder of either zinc borate or a mixture of aluminum trihydrate and zinc borate in a weight ratio of from about 4.5 to 35 parts per hundred of the composition, the weight ratio of zinc borate to aluminum trihydrate being not less than 1:6; added water in an amount between 30 and 45 parts per hundred of the composition; a thickening agent present in amount sufficient to maintain the powder in suspension; and a dispersing agent present in sufficient amount to impart fluidity to the composition and to enhance dispersion of the powder in the composition.</p>		

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## Fire Retardant Composition

This invention relates to coatings based on polymeric resins and more particularly to fire-retardant coating compositions.

5 A distinction should be made among fire or flame resistance and fire or flame retardancy. For purposes of the present invention, flame-resistant materials are defined as those that will not burn on contact with a flame, or if ignited, will not propagate the flame. For example, under ordinary atmospheric, temperature and pressure conditions, ceramic, cementitious and structural metal materials are considered  
10 to be flame resistant.

Fire retardant materials, for purposes of the present invention, are those that when exposed to a  
15 flame in an appropriate oxidizing atmosphere, will ignite, but will propagate the flame reluctantly or very slowly. Examples of such materials are the synthetic polymer-based formulations described in U.S. Patents 3,121,067; 3,287,312; 3,514,424; 3,524,761;  
20 3,524,901; 3,699,041; 3,748,317; 3,766,065; 3,783,133; 3,816,367; 3,897,387; 3,940,549; 4,191,675; 4,225,649; 4,243,579; 4,341,381; 4,430,470; 4,464,495; and many others. It is apparent that the use of polymeric coatings on flammable substrates to inhibit flame  
25 spread is old in the art.

Such coatings as are based upon silicone rubbers or fluorocarbons impart good fire retardancy, but tend to be expensive and do not adhere well to many substrates. Coatings based on epoxy resins tend to be  
30 rigid and are difficult to apply, at least in the

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field, in a thin layer to a substrate. Phenolic-based formulations tend to form a rigid char that does not adhere well. Polyurethanes, in addition to exhibiting poor thermal stability, may form toxic degradation products upon exposure to flames.

5 Particularly, such diverse organizations as the single-ply roofing industry, the Federal Aviation Agency, and the U.S. Navy, among others, have been searching for improved materials for reduction of flame spread and the prevention or reduction of the danger of "flash over", indicating that there is a current need for an improved fire-retardant coating.

10 It is, therefore, a primary object of the present invention to provide an improved fire-retardant, polymer-based coating composition that can be applied to various flammable substrates to provide reduced flame spread. It is another object of the present invention to provide a coating composition of the character described, which composition exhibits good adhesion to a variety of substrates, provides regulated gas escape, and assists in the formation of non-burning char. Still a further object of the present invention is to provide a coating composition of the character described that is relatively inexpensive, has good environmental stability and can be prepared and applied with ease using conventional equipment. Other objects of the present invention will in part be obvious and will in part appear hereinafter.

25 The invention, therefore, comprises the composition possessing the features, properties and the

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constituents, and the article of manufacture possesses the characteristics, properties and relation of elements, all as exemplified in the detailed disclosure hereinafter set forth and the scope of the invention of which will be indicated in the claims.

Accordingly, in one aspect of the present invention, there is provided a coating composition suitable for application to a flammable substrate for forming thereon a fire-retardant coating. The composition generally comprises an intimate mixture of a water emulsion of an ethylene-vinyl chloride copolymer with a finely powdered or comminuted zinc borate or a mixture of powdered aluminum trihydrate and zinc borate. The formulation preferably also optionally contains a thickener to maintain the powdered material in suspension, and an agent to impart fluidity and enhance dispersing action.

The foregoing fluid composition possesses a number of advantageous characteristics. Because it is water based, the coating equipment used to apply it to a substrate can be cleaned simply with soap and water and requires no expensive, possibly toxic or explosive, organic cleaning solvents. The composition of the invention dries at room temperature in a manner quite similar to the drying of latex paint, and forms a flexible coat that can, within reasonable limits, expand, contract and bend with the substrate.

The formulation is simply prepared by thoroughly mixing the ethylene-vinyl chloride copolymer, preferably in emulsion or latex form, with the inorganic

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powder, water and the thickening and dispersing agents. The powder is zinc borate with or without admixed aluminum trihydrate, added in a weight amount that can vary from as little as 4.5 to 32 parts per hundred of the final composition. The weight ratio of zinc borate in any such mix should be not less than 1:6 to the aluminum trihydrate. A known thickener such as cross-linked acrylic copolymer emulsion, gum, cellulose derivative or the like, is used to limit settling of the powder and control viscosity. A preferred dispersing agent used is an alkali salt of a carboxylate polyelectrolyte, typically the proprietary agent known as Tamol 850, which when mixed in the composition in minor and discretionary amount serves to enhance dispersion of the inorganic powder throughout the mixture and to impart fluidity to the mixture. In this mixture, the use of zinc borate or aluminum trihydrate-zinc borate mix imparts a significant reduction in flame response over the use of the ethylene-vinyl chloride/acrylic binder alone or the binder mixed with only aluminum trihydrate.

In a preferred embodiment, an ethylene-vinyl chloride copolymer emulsion is compounded with the thickener, typically an acrylic emulsion, in a ratio, by weight, of about 20:1, but this ratio can vary between about 10:1 to 50:1. A typical composition of the present invention of 100 parts by weight of the final composition, contains between 30 and 35 parts of the mixed emulsions, between 30 and 45 parts of water, between 30 and 35 parts of the zinc borate or zinc



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borate/aluminum trihydrate mix, and between 0.3 and 0.6 parts of the dispersing agent, if desired. Inasmuch as these weight percentages are based upon an emulsion that is nominally 50% by weight water and a thickener that is 70% by weight water, the dry weight percentages of ethylene-vinyl chloride and thickener in one hundred parts by weight of the final composition, can range from about 15/0.2 to 17/1 parts ethylene-vinyl chloride/thickener. One preferred embodiment then contains by weight about 33 parts mixed emulsions, about 40 parts of water, about 30.1 parts zinc borate or zinc borate/aluminum trihydrate and about 0.5 parts of the dispersing agent. In the preferred embodiment, the powder or pigment is a mixture of aluminum trihydrate and zinc borate in about a 3:1 weight ratio.

The foregoing composition exhibits a viscosity similar to that of an ordinary latex paint, and can be applied by any of the methods known for applying such paint, e.g., spraying, brushing, dipping, and the like.

The following examples, which are meant to be illustrative and not limiting, are provided to further describe the present invention and to detail the performance characteristics under test conditions for a coating formed by drying the present composition on a substrate. In all of the examples, the parts given are by weight.

#### EXAMPLE I

A coating mix is prepared by compounding in a

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mixer the following formulation in parts by weight:

water -- 271.5,  
aluminum trihydrate -- 207.3,  
zinc borate -- 69.1,

5 ethylene-vinyl chloride copolymer  
emulsion (50% percent water) -- 303.9,  
acrylic emulsion (70% percent water) -- 15.2.

The order in which materials are added to the  
mixer is not important with respect to the fire retar-  
10 dant properties attained, but to obtain good disper-  
sion, the mixture should be made in the following  
order: water, dispersant, powdered inorganics, ethylene-  
vinyl chloride emulsion and thickener. The mixture  
was agitated for sufficient time to obtain a smooth,  
15 complete dispersion of the materials with respect to  
one another. The final mixture was applied to a test  
strip (12" long) of unsized, uncoated closely-woven  
cotton muslin (2.5 oz/yd<sup>2</sup>) by passing the latter  
through a size press nip at which the coating was  
20 introduced. The coated muslin was permitted to dry  
and the coated material thereon constituted approxima-  
tely 15 percent by weight of the dried, coated fabric.

The coated fabric was subject to testing in  
accordance with ASTM F501-77 to provide the following  
25 results:

<u>FLAME TIME</u>	<u>AFTER GLOW TIME</u>	<u>BURN LENGTH</u>
(Sec.)	(Sec.)	(In.)
0	0	4

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EXAMPLE II

A formulation was prepared substantially as set forth in Example I, omitting zinc borate and using 276.4 parts of aluminum trihydrate instead of the mixture of the two inorganic materials. A test strip of the same cotton muslin was coated in the same manner with the same weight percent of the formulation and subjected to the same flame test with the following results:

	<u>FLAME TIME</u>	<u>AFTER GLOW TIME</u>	<u>BURN LENGTH</u>
	(Sec.)	(Sec.)	(In.)
	16.8	0	12 (entire)

EXAMPLE III

A coating formulation was prepared in the same manner and proportions as set forth in Example I except that no aluminum trihydrate was used, the amount of zinc borate being adjusted to 276.4 parts. sodium salt of a carboxylate polyelectrolyte -- 4.6, As described in Example I, a muslin strip was coated but with the formulation of Example III to provide the same weight percentage of dried coating. The dried, coated strip was subjected to the same test with the following results:

	<u>FLAME TIME</u>	<u>AFTER GLOW TIME</u>	<u>BURN LENGTH</u>
	(Sec.)	(Sec.)	(In.)
	0	0	4.8

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EXAMPLE IV

A formulation was prepared in accordance with the procedure and amounts as set forth in Example I except that the ratio of aluminum trihydrate to zinc borate was changed to 6:1. A muslin strip was coated in accordance with the procedure and dried to provide a coated substrate of the same weight percent coating as in the preceding Examples, and when tested in the same test, yielded the following results:

	<u>FLAME TIME</u>	<u>AFTER GLOW TIME</u>	<u>BURN LENGTH</u>
	(Sec.)	(Sec.)	(In.)
	3.75	0	6.5

EXAMPLE V

As a comparative basis for the tests conducted in the four preceding Examples, a strip of the uncoated, unsized 2.5 oz/yd<sup>2</sup> close-weave cotton muslin was subjected to the same test with the following results:

	<u>FLAME TIME</u>	<u>AFTER GLOW TIME</u>	<u>BURN LENGTH</u>
	(Sec.)	(Sec.)	(In.)
	Not applicable	300	12 (entire)

From the results determined from the preceding Examples, it is apparent the present formulation yields a substantially superior flame-retardant coating.

While the composition of the invention has been described, in the examples, as being applied to cotton fabric, it is to be understood that it may be applied to a wide variety of substrates possessing various degrees of flammability, for example, wood and other cellulosic sheathing, foamed polyurethanes and nitri-

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les, fabrics, calendered polymeric sheeting and boards, and the like.

5 It will thus be seen that the objects set forth above, among those made apparent by the preceding description, are efficiently obtained. Since certain changes may be made in the composition and articles set forth in the examples, without departing from the scope of this invention, it is intended that all matter contained in the above description shall be  
10 interpreted as illustrative and not in a limiting sense.

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WHAT IS CLAIMED IS:

1           1. A coating composition suitable for applica-  
2           tion to a substrate for curing thereon to form a fire-  
3           retardant coating, said composition comprising in  
4           combination

5           an aqueous emulsion of ethylene-vinyl chloride  
6           copolymer, the ratio of the dry weight of said copo-  
7           lymer to one hundred parts of the composition being in  
8           the range between about 15 to 17 parts; and

9           dispersed in said emulsion, finely divided zinc  
10          borate or a mixture of aluminum trihydrate and zinc  
11          borate in a weight ratio of from about 4.5 to 35 parts  
12          per hundred of said composition, the weight ratio of  
13          zinc borate to aluminum trihydrate in said mixture  
14          being not less than 1:6.

1           2. A composition as defined in claim 1 including  
2           added water in an amount between 30 and 45 parts per  
3           hundred of said composition.

1           3. A composition as defined in claim 2 including  
2           a thickening agent present in amount sufficient to  
3           maintain said finely divided zinc borate or zinc  
4           borate/aluminum trihydrate in suspension in said composition.

1           4. A composition as defined in claim 3 wherein  
2           said thickening agent is present, in a ratio, by dry  
3           weight, of between approximately 0.2 to 1 part per  
4           hundred of said composition.

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1           5. A composition as defined in claim 3 wherein  
2 said thickening agent is a cross-linked acrylic copo-  
3 lymer emulsion.

1           6. A composition as defined in claim 2 including  
2 a dispersing agent present in sufficient amount to  
3 impart fluidity to said composition and to enhance  
4 dispersion of said finely divided zinc borate or zinc  
5 borate/aluminum trihydrate in said composition.

1           7. A composition as defined in claim 6 wherein  
2 said dispersing agent is present in about 0.3 to 0.6  
3 weight percent of said composition.

1           8. A composition as defined in claim 6 wherein  
2 said dispersing agent is an alkali salt of a car-  
3 boxylate polyelectrolyte.

# INTERNATIONAL SEARCH REPORT

International Application No

PCT/US 86/01614

<b>I. CLASSIFICATION OF SUBJECT MATTER</b> (if several classification symbols apply, indicate all) <sup>3</sup>		
According to International Patent Classification (IPC) or to both National Classification and IPC		
IPC4 C09K 21/00; C09D 5/18; C08K 3/38 US 252/610, 609, 310, 313.1; 106/18.27, 18.13		
<b>II. FIELDS SEARCHED</b>		
Minimum Documentation Searched <sup>4</sup>		
Classification System	Classification Symbols	
US	252/601, 607, 608, 609, 610, 611, 310, 313.1; 106/18.27, 18.13; 524/845	
Documentation Searched other than Minimum Documentation to the Extent that such Documents are Included in the Fields Searched <sup>5</sup>		
USPAT word search		
<b>III. DOCUMENTS CONSIDERED TO BE RELEVANT</b> <sup>14</sup>		
Category <sup>*</sup>	Citation of Document, <sup>15</sup> with indication, where appropriate, of the relevant passages <sup>17</sup>	Relevant to Claim No. <sup>18</sup>
Y	US, A, 3985706 Published 12 October 1976 Kay "see Summary of Invention"	1-8
Y	US, A, 4097630 Published 27 June 1978 Schwartz, et al "see entire document"	1-8
Y	JP, A, 58/041972 Published 11 March 1983 "see Derwent abstract"	1-8
A	US, A, 3770577 Published 6 November 1973 Humphrey "see entire document"	1-8
<p><sup>*</sup> Special categories of cited documents: <sup>15</sup></p> <p>"A" document defining the general state of the art which is not considered to be of particular relevance</p> <p>"E" earlier document but published on or after the international filing date</p> <p>"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)</p> <p>"O" document referring to an oral disclosure, use, exhibition or other means</p> <p>"P" document published prior to the international filing date but later than the priority date claimed</p> <p>"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention</p> <p>"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step</p> <p>"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.</p> <p>"&amp;" document member of the same patent family</p>		
<b>IV. CERTIFICATION</b>		
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